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Report Title

Fabrication and Test of MC/BZY Proton Conductor

ABSTRACT

Technical report of 2013-2014 (experimental part)

Novel MC/BZY Proton Conductor: Materials Development, Device Evaluation, and Theoretical Exploration using CI and DFT Methods

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(Experimental Part)

I. Experimental procedures

1. Infiltration of molten carbonates into porous BZY pellets

1.1 Fabrication of Porous BZY Pellets

BZY ($BaZr_{0.8}Y_{0.2}O_{2.9}$) electrolyte was made by classical solid state reaction. The staring precursors for BZY are $BaCO_3$ (99.8%, Alfa Aesar), ZrO_2 (99.7%, Alfa Aesar) and Y_2O_3 (99.9%, Alfa Aesar). After weighing and mixing, calcinations were first carried out at 1100°C for five hours. The calcined samples were then broken up into powders and calcined at 1300℃ for another five hours, followed by grinding down to fine powders. Proportional carbon black, as pore former, was added into the as-prepared BZY powder before dry pressing. Additional burn-out processing was carried out at 400℃ for 2 hours and 600℃ for 2 hours, respectively. Finally, BZY pellets were sintered at 1500℃ for 5 hours and ready for molten carbonate infiltration.

1.2 Synthesis of Molten Carbonate and Infiltration

Li/K and Li/Na carbonate were prepared by melting lithium carbonate (99%, Alfa Aesar) and potassium carbonate (99%, Alfa Aesar) in 62:38 (mol%), lithium carbonate (99%, Alfa Aesar) and sodium carbonate (99%, Alfa Aesar) in 52:48 (mol%) at 650°C for 2 hours. The as-prepared BZY pellets were loaded into a silver basket and immersed into the molten carbonate for 2 hours, and then pulled out of the melts before they were cooled down to room temperature. Thus fabricated MC/BZY composites were then slightly polished on the surfaces to remove the residual melt. All the pellets were ready for electrochemical impedance measurement.

2 Characterization of MC/BZY

The sintered BZY powders were examined by X-ray diffraction (XRD) patterns to confirm the formation of BZY, while the microstructures of BZY pellets as well the MC/BZY composites were observed by a field emission scanning electron microscopy (SEM).

Ionic conductivity of MC/BZY composites were measured by electrochemical impedance spectroscopy. Before measurement, MC/BZY pellets were made to be a symmetrical cell configuration with Ag as the electrode. To study ionic conductivity of MC/BZY composites, air contained 3% H_2O, and 5% hydrogen in nitrogen containing 3% H_2O, represented as the atmosphere of cathode and anode, respectively, were used in the temperature range of 400 to 650℃. For the study of the effect of H_2O partial pressure on ionic conductivity, gas was passed through a water saturator at fixed temperature. A humidity sensor (Vaisala model 332) was used to measure the real steam content in the gas.

II. Results and Discussion

1 XRD Examinations and Microstructural Features

The XRD pattern shown in Fig.1 indicates a single cubic perovskite structure for BZY after calcining at 1300℃ for 5 h.

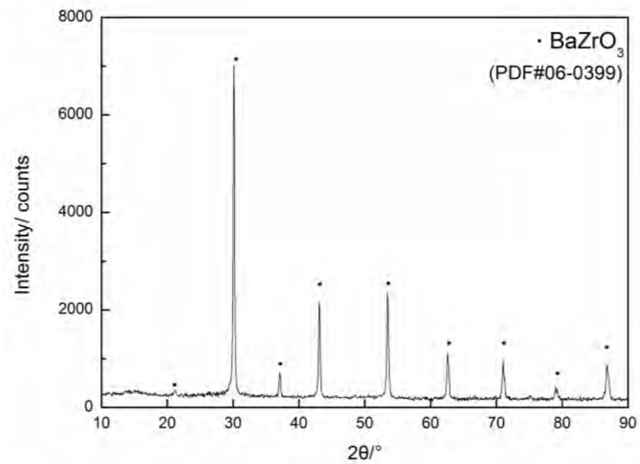

Fig.1 XRD pattern of BZY

The microstructures of porous BZY and MC/BZY composite are shown in Fig.2 (a) and (b). Before infiltration, BZY pellets appear to be non-uniform in grain size and poorly connected. In contrast, Fig.2 (c) and (d) show that the MC/BZY composite is dense and crack free after infiltration with carbonate well dispersed within BZY grains.

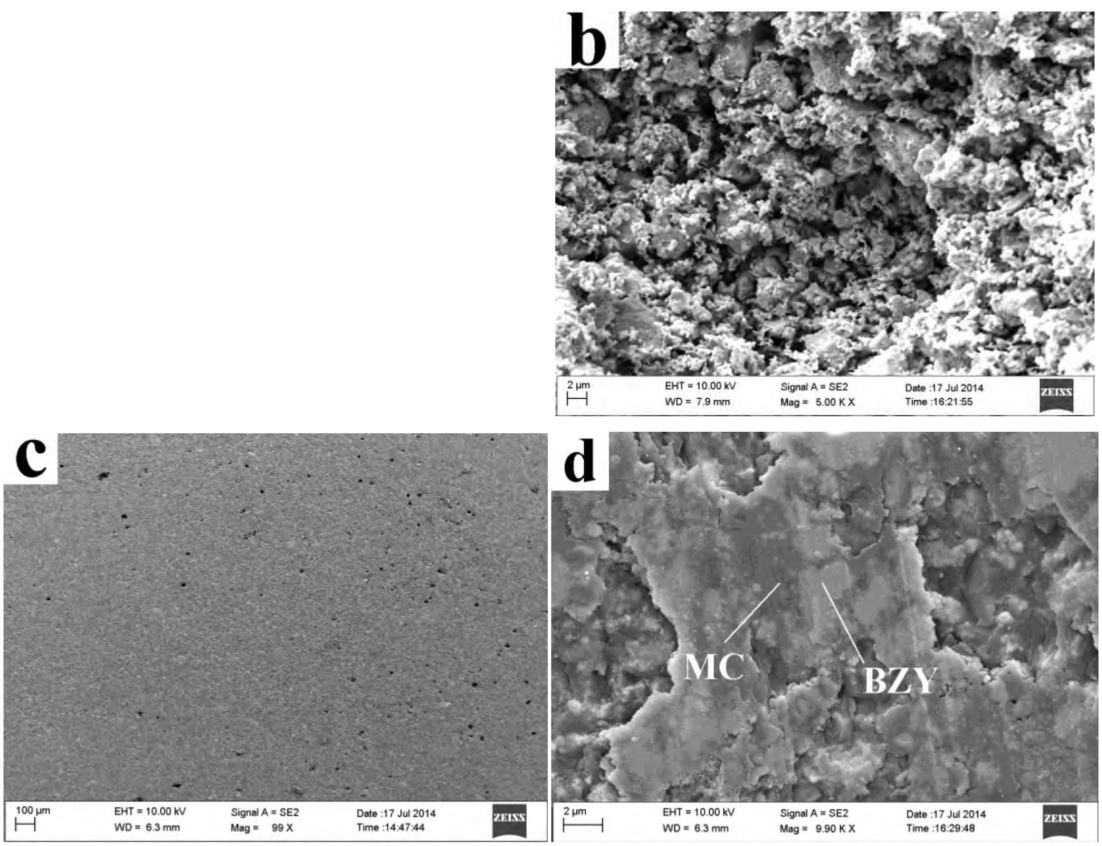

Fig.2 SEM image of (a) surface and (b) fracture of BZY sintered at 1500^{o}C; (c) and (d) fracture surface of Li-Na carbonate/BZY composite fired at 650^{o}C

2 The Effects on Conductivity

It is found that higher MC loading leads to a higher conductivity. Different amount of carbon black were added to BZY powder to create different porosities, which has resulted in an obvious difference in Li_2CO_3-K_2CO_3 (62:38 mol%) loading as shown in Fig.3. The conductivity of samples with higher MC loading is higher below 490^{o}C when carbonate is in solid state, while the difference is less apparent above 490^{o}C.

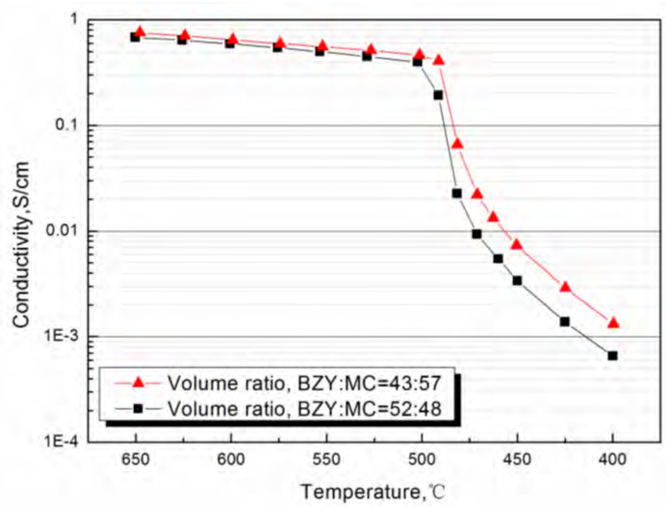

Fig.3 Plots of conductivity as a function of temperature in 3%H_2O-air of MC/BZY composites with different MC loading

Different alkaline composition of MC also affected specimen's conductivity. For a BZY sample with the same porosity infiltrated with Li_2CO_3-K_2CO_3 (62:38 mol%) and Li_2CO_3-Na_2CO_3 (52:48 mol%), the results shown in Fig. indicate that the sample infiltrated with Li_2CO_3-Na_2CO_3 (52:48 mol%) has a higher conductivity at > 500^{o}C. This observation is consistent with that Li-Na carbonate has a higher conductivity that Li-K carbonate.

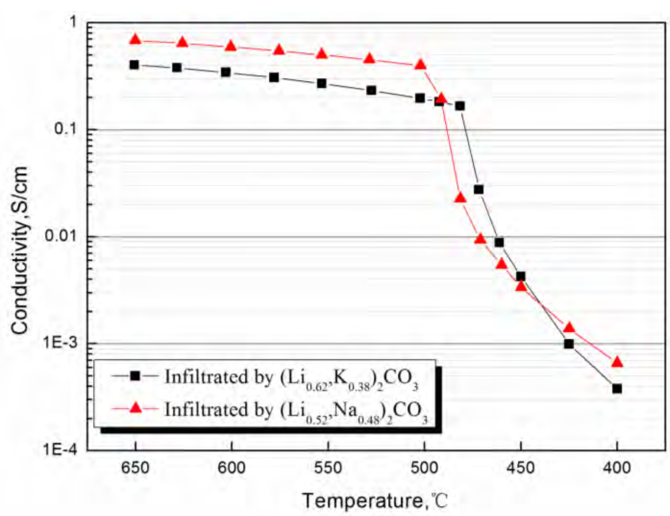

Fig.4 Plots of conductivity as a function of temperature in 3%H_2O-air of BZY pellets with the same porosity and infiltrated by Li/K and Li/Na carbonates

It is also found that the conductivity is higher in wet hydrogen than in wet air. BZY pellets with the highest porosity were infiltrated by Li_2CO_3-Na_2CO_3 (52:48 mol%), resulting in a MC loading as of 57 vol%. As indicated in Fig.5, the conductivity in 3%H_2O-H_2 is higher than that in 3%H_2O-air over the whole temperature range, but difference was larger below 490^oC. As a reference, the conductivity of pure Li_2CO_3-Na_2CO_3 (52:48 mol%) was presented, which indicated the highest conductivity possible. A set of reference conductivity for the MC/BZY composite at 600^oC is 1.11 S/cm for 3%H_2O-H_2 and 0.65 S/cm for 3%H_2O-air.

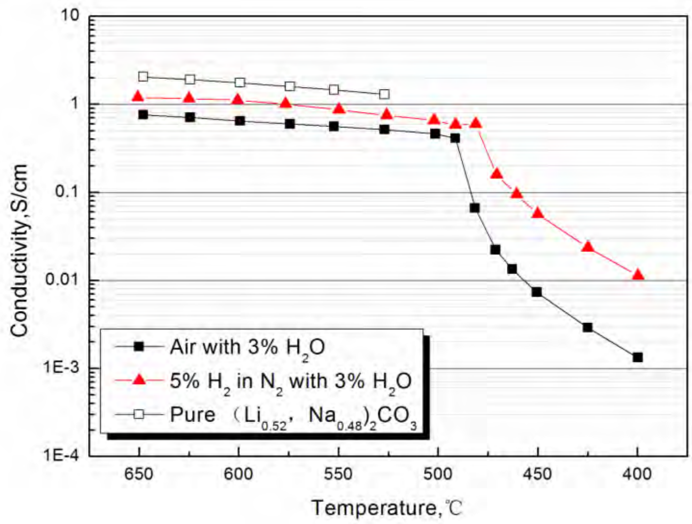

Fig. 5 Plots of conductivity as a function of temperature in 3%H_2O-air and in 3%H_2O-H_2 of Li-Na carbonate/BZY composite sample

The conductivity is found to increase with humidity in H_2. The isothermal conductivity of a MC/BZY composite with the highest Li_2CO_3-Na_2CO_3 (52:48 mol%) loading was measured as a function of partial pressure of H_2O (P_{H2O}) at 600^oC, as shown in Fig.6. Compared to those measured in air, the conductivity measured in hydrogen was almost twice higher and it appeared to linearly increase with P_{H2O} in both atmospheres.

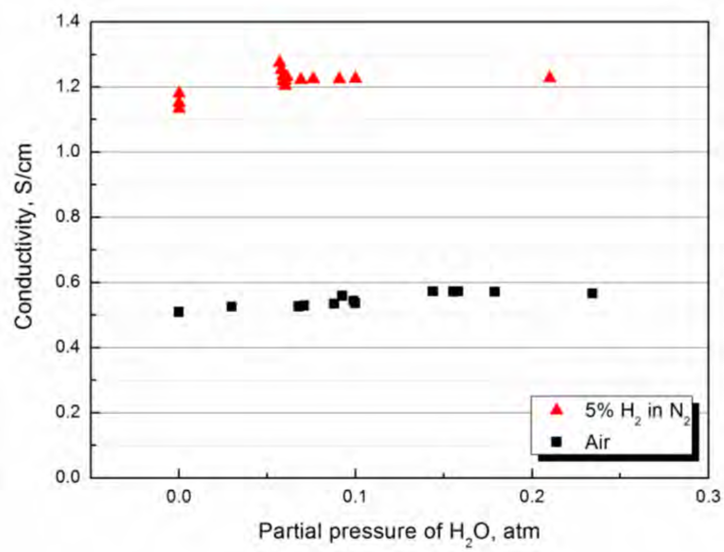

Fig. 6 Plots of conductivity as a function of P_{H2O} of Li-Na carbonate/BZY composite

III. Conclusion and next step

In summary, the BZY/MC composite ionic conductor has been characterized microstructurally and electrochemically. It was found that the original porous BZY pellets become dense after being filled with molten carbonates. The conductivity shows a sharp increase at the solid-liquid phase transformation temperature. The conductivity of BZY/MC composite ionic conductor increases with lower partial pressure of oxygen and higher humidity.

During the next reporting period, we will focus on study of developing compatible electrode materials for MC/BZY and electrochemical testing of MC/BZY based SOFCs and SOECs.